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Density functional calculations of molecular g -tensors in the zero-order regular approximation for relativistic effects

Erik van Lenthe, Paul E. S. Wormer, and Ad van der Avoird

Institute of Theoretical Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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A method has been developed for the calculation of the g -tensor of Kramers doublet open shell molecules, which uses the spinor of the unpaired electron of the paramagnetic molecule, obtained from a density functional calculation. Spin-orbit coupling is taken into account variationally using the zeroth-order regular approximation (ZORA) to the Dirac equation. The problem of gauge dependence is solved by using gauge including atomic orbitals (GIAO's). The method gives fair agreement with experimental values for the g values of some small test molecules NO_2 , HCO , and TiF_3 . © 1997 American Institute of Physics. [S0021-9606(97)05131-3]

I. INTRODUCTION

The effective spin Hamiltonian is an important model for the interpretation of electron spin resonance (ESR) experiments. In this Hamiltonian the molecular g -tensor parametrizes the interaction between the effective magnetic spin of the paramagnetic molecule of interest and the external homogeneous magnetic field. For many systems spin-orbit coupling is the most important factor for shifting the g -values away from the free electron value g_e . In standard approaches the g -tensor is often calculated by means of second order perturbation theory¹⁻⁴ or finite perturbation theory,⁵ which both include the effect of spin-orbit coupling only in first order. In this article we want to take spin-orbit coupling into account variationally. For the effect of the external homogeneous magnetic field we then only need simple first order perturbation theory (FOPT).

We will follow the discussion of Abragam and Bleaney⁶ for a paramagnetic molecule, which has a (Kramers) doublet ground state if no magnetic field is present. In their discussion the difference between the fictitious spin of the spin Hamiltonian and a real electronic spin is clearly explained. The Kramers doublet is used to determine the magnetic Hamiltonian. We will use density functional theory (DFT), employing the usual (nonrelativistic) density functionals for the exchange-correlation energy: local density functionals (LDA) with gradient correction (GGC) terms added, namely the Becke correction for exchange⁷ and the Perdew correction for correlation.⁸ We will use spin-restricted density functionals, since spin-polarization effects in spin-orbit coupled equations are difficult to calculate, see for example Ref. 9. An interesting idea in this respect can be found in, for example,^{10,11} where the inclusion of spin-polarization effects in spin-orbit coupled equations leads to off-diagonal elements in the exchange-correlation potential.

In the present paper spin-orbit coupling will be included in the zeroth-order regular approximation (ZORA)¹²⁻¹⁴ to the Dirac equation. The regular expansion, which leads to the ZORA Hamiltonian, remains valid even for a Coulombic potential. This is in contrast with the expansion that leads to the Pauli-Hamiltonian, which is divergent for a Coulombic po-

tential. The regular expansion was already used in the book of Harriman² from 1978 on theoretical foundations of ESR. The ZORA Hamiltonian is then the zeroth order of what Harriman calls the modified partitioning of the Dirac equation. Later work on the regular expansion by Chang *et al.*¹² and Heully *et al.*¹³ appeared in 1986.

It was shown in Ref. 15, that the ZORA Hamiltonian is bounded from below for Coulombic potentials. Exact solutions for the hydrogenic ions were given and in Ref. 16 it was shown that the scaled ZORA energies in that case are exactly equal to the Dirac energies. In Ref. 9 the ZORA Hamiltonian has been successfully applied in spin-orbit coupled relativistic calculations on molecules, by means of density functional theory.

Relativistic regular approximated expressions for magnetic interactions will be derived in Sec. II, and will be used for the Zeeman term in Sec. III, where the link with the effective spin Hamiltonian will be given.

In Sec. IV A details are given for the calculation of matrix elements using a single gauge origin for the magnetic field. If one uses a finite basis set, the results for the calculation of the g -values depend on the gauge origin chosen for the magnetic field. This problem is solved in Sec. IV B by the use of gauge including atomic basis functions (GIAO's), see Refs. 17 and 18.

In Sec. VI the results for the g -tensor of NO_2 , HCO , and TiF_3 will be given, and we will study the basis set dependence, the frozen core approximation and the gauge dependence.

II. THEORY

In this section nonrelativistic, relativistic, and some approximate relativistic equations containing an external magnetic field are compared. Expressions for the zeroth-order regular approximation (ZORA) to the Dirac equation are derived. Note that these expressions are very similar to the results of the modified partitioning of the Dirac equation used by Harriman.² Differences with his approach are the order in which some terms appear, and the fact that we use the scaled ZORA energy expression, which is a great im-

provement over the already accurate ZORA energy.¹⁶ Since we will use density functional theory we will consider here only one-electron equations. The effective Kohn–Sham potential used in our calculations is the sum of the nuclear potential, the Coulomb potential due to the total electron density and the exchange–correlation potential, for which we will use nonrelativistic approximations.

A. Electric field

If only a time-independent electric field is present, the nonrelativistic and some relativistic one-electron equations can be written in atomic units ($\mathbf{p} = -i\nabla$), by the use of an auxiliary function K , as

$$\left[V + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{p} \right] \Psi = E \Psi. \quad (1)$$

Here use is made of the identity

$$(\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i \boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}) \quad (2)$$

for the Pauli spin matrices $\boldsymbol{\sigma}$.

The auxiliary function K , which determines whether the equation is relativistic, and the electrostatic potential V are functions that depend only on \mathbf{r} , the position of the electron, defined in some arbitrary coordinate system. We will use the $-i\nabla$ form for \mathbf{p} to indicate that the gradient only works on the function next to it.

For $K = 1$ Eq. (1) is the ordinary nonrelativistic Schrödinger equation

$$[V + \frac{1}{2}p^2]\Psi = E\Psi. \quad (3)$$

For $K = [1 + (E - V)/2c^2]^{-1}$ this equation is the Dirac equation for the large component Ψ^L of the Dirac wave function, which one obtains after the elimination of the small component Ψ^S in the Dirac equation

$$\left[V + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{2c^2 + E - V} \boldsymbol{\sigma} \cdot \mathbf{p} \right] \Psi^L = E \Psi^L, \quad (4)$$

where E is the orbital energy of the electron, and c the velocity of light (in a.u. $c \approx 137.035\,989\,5$). The small component is related to the large component by

$$\Psi^S = \frac{c}{2c^2 + E - V} \boldsymbol{\sigma} \cdot \mathbf{p} \Psi^L. \quad (5)$$

For $K = [1 - V/2c^2]^{-1}$ we have the ZORA equation, the zeroth order of the regular expansion of the Dirac equation

$$\left[V + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{2c^2 - V} \boldsymbol{\sigma} \cdot \mathbf{p} \right] \Psi^{\text{ZORA}} = E^{\text{ZORA}} \Psi^{\text{ZORA}}. \quad (6)$$

An improved one-electron energy can be obtained by using the scaled ZORA energy expression

$$E^{\text{scaled}} = \frac{E^{\text{ZORA}}}{1 + \langle \Psi^{\text{ZORA}} | \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{(2c^2 - V)^2} \boldsymbol{\sigma} \cdot \mathbf{p} | \Psi^{\text{ZORA}} \rangle}. \quad (7)$$

To obtain the Pauli equation one can roughly use $K = 1 - (E - V)/2c^2$, but then one should be careful about removing the energy dependence in the resulting equation. A more systematic approach is the Foldy and Wouthuysen transformation,¹⁹ which decouples the large and small components of the Dirac equation to successively higher orders of c^{-2} . Up to order c^{-2} one then obtains the Pauli equation

$$\left[V + \frac{1}{2}p^2 - \frac{1}{8c^2}p^4 + \frac{1}{8c^2}\nabla^2 V + \frac{1}{4c^2}\boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}) \right] \Psi = E \Psi. \quad (8)$$

B. Electromagnetic field

We will now consider the (non-) relativistic equation if also a time-independent magnetic field is present. If we make the usual minimal substitution for a negatively charged particle

$$\mathbf{p} \rightarrow \boldsymbol{\Pi} = \mathbf{p} + \frac{\mathbf{A}}{c}, \quad (9)$$

where \mathbf{A} is the vector potential, we obtain the (non-) relativistic one-electron equation including a magnetic field

$$\left[V + \boldsymbol{\sigma} \cdot \boldsymbol{\Pi} \frac{K}{2} \boldsymbol{\sigma} \cdot \boldsymbol{\Pi} \right] \Psi = E \Psi. \quad (10)$$

For $K = 1$ we have the nonrelativistic Levy–Leblond equation^{20,21}

$$V + \frac{1}{2}(\boldsymbol{\sigma} \cdot \boldsymbol{\Pi})^2 = V + \frac{1}{2}\boldsymbol{\Pi}^2 + \frac{1}{2c}\boldsymbol{\sigma} \cdot \mathbf{B}, \quad (11)$$

where $\mathbf{B} = \nabla \times \mathbf{A}$ is the magnetic field.

Again for $K = [1 + (E - V)/2c^2]^{-1}$ Eq. (10) is the Dirac equation, for the large component of the Dirac wave function, and for $K = [1 - V/2c^2]^{-1}$ it is the ZORA equation. The scaled ZORA energy expression becomes

$$E^{\text{scaled}} = \frac{E^{\text{ZORA}}}{1 + \langle \Psi^{\text{ZORA}} | \boldsymbol{\sigma} \cdot \boldsymbol{\Pi} \frac{c^2}{(2c^2 - V)^2} \boldsymbol{\sigma} \cdot \boldsymbol{\Pi} | \Psi^{\text{ZORA}} \rangle}. \quad (12)$$

The operator in Eq. (10) can further be written out as

$$\begin{aligned} V + \boldsymbol{\sigma} \cdot \boldsymbol{\Pi} \frac{K}{2} \boldsymbol{\sigma} \cdot \boldsymbol{\Pi} &= V + \boldsymbol{\Pi} \cdot \frac{K}{2} \boldsymbol{\Pi} + \frac{K}{2c} \boldsymbol{\sigma} \cdot (\nabla \times \mathbf{A}) + \boldsymbol{\sigma} \cdot \left(\left[\nabla \frac{K}{2} \right] \times \boldsymbol{\Pi} \right) \\ &= V + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{p} + \frac{K}{2c} \mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A} \frac{K}{2c} \\ &\quad + \frac{K}{2c^2} A^2 + \frac{K}{2c} \boldsymbol{\sigma} \cdot \mathbf{B} + \boldsymbol{\sigma} \cdot \left(\nabla \frac{K}{2c} \times \mathbf{A} \right). \end{aligned} \quad (13)$$

For the Pauli approximation [roughly $K = 1 - (E - V)/2c^2$] one obtains besides the terms of Eq. (8) and the $\boldsymbol{\sigma} \cdot \mathbf{B}$ -term of the Levy-Leblond equation, some extra correction terms, such as

$$-\frac{1}{4c^3} p^2 \boldsymbol{\sigma} \cdot \mathbf{B} + \frac{1}{4c^3} \boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{A}). \quad (14)$$

These are called respectively the spin-Zeeman kinetic-energy correction (relativistic mass correction to the spin-Zeeman term) and the one-electron spin-orbit Zeeman gauge correction^{2,22} in the Pauli approximation. One can find similar terms in the ZORA equation, if one expands the function K in c^{-2} . If one expands the scaled ZORA energy expression in c^{-1} , the terms up to order c^{-3} will give exactly the Pauli approximation. Note that the spin-orbit Zeeman gauge correction does not depend on the orbital angular momentum. It can also be taken into account in a scalar relativistic equation, i.e., an equation without the spin-orbit operator.

Due to quantum electrodynamic effects the $\boldsymbol{\sigma} \cdot \mathbf{B}$ term in Eq. (13) obtains an extra factor $g_e/2$

$$\frac{g_e}{2c} \frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{B}, \quad (15)$$

where g_e is the free electron *g*-value ($\approx 2.002\,319\,31$). The last term in Eq. (13), which is the spin-orbit Zeeman gauge correction in the Pauli approximation, is also modified by quantum electrodynamic effects²

$$\frac{g'_e}{2c} \boldsymbol{\sigma} \cdot \left(\nabla \frac{K}{2} \times \mathbf{A} \right). \quad (16)$$

Although g_e and g'_e differ slightly, we will make the approximation that $g'_e = g_e$, and this difference will only result in a small correction to the already small spin-orbit Zeeman gauge correction. We will conveniently multiply the other terms linear in \mathbf{A} with a factor $g_e/2$

$$\frac{g_e}{2c} \frac{K}{2} \mathbf{A} \cdot \mathbf{p} + \frac{g_e}{2c} \mathbf{p} \cdot \mathbf{A} \frac{K}{2}, \quad (17)$$

which is a small modification since g_e is close to two.

III. THE EFFECTIVE SPIN HAMILTONIAN

Suppose we have a paramagnetic molecule in an external homogeneous magnetic field B^0 . The electronic Zeeman interaction H^Z may be effectively written as

$$H^Z = \mathbf{B}^0 \cdot \frac{\mathbf{g}}{2c} \cdot \tilde{\mathbf{S}}. \quad (18)$$

The molecular *g*-tensor parametrizes the interaction between the effective magnetic spin $\tilde{\mathbf{S}}$ of the molecule and the external magnetic field. In this section the *g*-tensor will be considered theoretically.

In standard approaches the effect of spin-orbit coupling is included only in first order, whereas in our approach spin-orbit coupling is taken into account variationally. This approach is also valid for the Dirac equation, since this equation contains spin-orbit coupling. The effect of spin-orbit

coupling can be large if heavy atoms are present in the molecule. For example for transition metal complexes spin-orbit coupling can be as important as the ligand-field splittings (deviations from spherical symmetry). The typical effects of the external homogeneous magnetic field are much smaller in that case.

The vector field \mathbf{A}^0 can be chosen as

$$\mathbf{A}^0 = \frac{1}{2}(\mathbf{B}^0 \times \mathbf{r}). \quad (19)$$

Different choices for \mathbf{A}^0 can be made, by choosing another origin for the vector \mathbf{r} , the position of the electron. The sum of the terms linear in the field in Eq. (13) form the Zeeman Hamiltonian H^Z ($\mathbf{L} = \mathbf{r} \times \mathbf{p}$)

$$H^Z = \frac{g_e}{2c} \left[\frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{B}^0 + \frac{K}{4} \mathbf{B}^0 \cdot \mathbf{L} + \mathbf{B}^0 \cdot \mathbf{L} \frac{K}{4} + \boldsymbol{\sigma} \cdot \left(\nabla \frac{K}{2} \times \mathbf{A}^0 \right) \right]. \quad (20)$$

The first term is the electron spin Zeeman term, the next two terms form the orbital Zeeman interaction and the last term is the spin-orbit Zeeman gauge correction, as they are called in the Pauli approximation.

Suppose we have an odd number of electrons in a molecule, and the ground level only has Kramers degeneracy. We now follow the discussion of Abragam and Bleaney⁶ for the "spin Hamiltonian" of such a Kramers doublet, assuming that this doublet completely determines this magnetic Hamiltonian. We then only need to calculate the matrix elements of the Zeeman-Hamiltonian between the two degenerate spin-orbitals Φ_1 and Φ_2 , which are eigenfunctions of the Hamiltonian H_0 , without magnetic field [see Eq. (1)]

$$H_0 = V + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{p}. \quad (21)$$

These two spin-orbitals, which are connected by time-reversal symmetry, can be written as

$$\Phi_1 = \begin{pmatrix} \phi_a \\ \phi_b \end{pmatrix}, \quad \Phi_2 = \begin{pmatrix} -\phi_b^* \\ \phi_a^* \end{pmatrix}. \quad (22)$$

For the energy in first order in the magnetic field we can write

$$\frac{\partial}{\partial B_k^0} \begin{pmatrix} \langle \Phi_1 | H^Z | \Phi_1 \rangle & \langle \Phi_1 | H^Z | \Phi_2 \rangle \\ \langle \Phi_2 | H^Z | \Phi_1 \rangle & \langle \Phi_2 | H^Z | \Phi_2 \rangle \end{pmatrix} = \frac{1}{4c} \sum_l g_{kl} \sigma_l, \quad (23)$$

with real coefficients g_{kl} , since any Hermitian two-by-two matrix can be expressed as a linear combination of the three Pauli matrices and the unit matrix with real coefficients. There is no contribution of the unit matrix since the Zeeman-Hamiltonian is a time-odd operator, and hence the energy matrix is traceless. From the real numbers g_{kl} a true tensor G_{pq} can be made

$$G_{pq} = \sum_k g_{pk} g_{qk}. \quad (24)$$

This tensor can be made diagonal by a proper choice of coordinate axes. The eigenvalues of this matrix are the squares of the *g*-values.

In the regular approximation one also likes to use the scaled ZORA energy expression, since it is an improvement on the ZORA energy. We will approximate its effect by multiplying the matrix of Eq. (23) with a factor

$$\frac{1}{1 + \langle \Phi_1 | \boldsymbol{\sigma} \cdot \mathbf{p} \frac{1}{(2c^2 - V)^2} \boldsymbol{\sigma} \cdot \mathbf{p} | \Phi_1 \rangle} = \frac{1}{1 + \langle \Phi_2 | \boldsymbol{\sigma} \cdot \mathbf{p} \frac{1}{(2c^2 - V)^2} \boldsymbol{\sigma} \cdot \mathbf{p} | \Phi_2 \rangle}. \quad (25)$$

Thus in this approximation the scaled ZORA approach will give an isotropic decrease of the *g*-values compared to ZORA.

IV. EVALUATION OF THE *g*-TENSOR

In this section details are given on the matrix elements needed for the evaluation of the *g*-tensor. We start with a formulation, which uses a single gauge origin for the magnetic field. This formulation uses basis functions which do not depend on the external magnetic field. The results for the calculation of the *g*-values will depend on the gauge origin chosen for the magnetic field, if one uses a finite basis set. This problem of gauge dependence in a finite basis is solved in Sec. IV B by the use of gauge including atomic basis functions (GIAO's).

It is shown that if one starts with exact eigenfunctions of the Hamiltonian without magnetic field, there is no gauge dependence of the results, and that the formulation using a single gauge origin will then coincide with the formulation using GIAO's.

A. Single gauge origin

In this section we assume that we have calculated the Kramers pair Φ_1 and Φ_2 of Sec. III using a basis set consisting of functions which do not depend on the external magnetic field. For the *g*-tensor we need to calculate matrix elements of the derivative of the Zeeman-Hamiltonian with respect to B_k^0 , see Eq. (23)

$$\begin{aligned} g_{kx} &= 4c \operatorname{Re} \langle \Phi_1 | \frac{\partial}{\partial B_k^0} H^Z | \Phi_2 \rangle \\ &= 4c \operatorname{Re} \langle \Phi_2 | \frac{\partial}{\partial B_k^0} H^Z | \Phi_1 \rangle, \end{aligned} \quad (26a)$$

$$\begin{aligned} g_{ky} &= -4c \operatorname{Im} \langle \Phi_1 | \frac{\partial}{\partial B_k^0} H^Z | \Phi_2 \rangle \\ &= 4c \operatorname{Im} \langle \Phi_2 | \frac{\partial}{\partial B_k^0} H^Z | \Phi_1 \rangle, \end{aligned} \quad (26b)$$

$$\begin{aligned} g_{kz} &= 4c \operatorname{Re} \langle \Phi_1 | \frac{\partial}{\partial B_k^0} H^Z | \Phi_1 \rangle \\ &= -4c \operatorname{Re} \langle \Phi_2 | \frac{\partial}{\partial B_k^0} H^Z | \Phi_2 \rangle, \end{aligned} \quad (26c)$$

since Φ_1 and Φ_2 do not depend on \mathbf{B} , in our approximation. The derivative of the Zeeman-Hamiltonian with respect to B_k^0 is from Eq. (20),

$$\begin{aligned} \frac{\partial}{\partial B_k^0} H^Z &= \frac{g_e}{2c} \left[\frac{K}{2} \sigma_k + \frac{K}{4} L_k + L_k \frac{K}{4} + \left(\mathbf{r} \cdot \nabla \frac{K}{4} \right) \sigma_k \right. \\ &\quad \left. - (\boldsymbol{\sigma} \cdot \mathbf{r}) \nabla_k \frac{K}{4} \right]. \end{aligned} \quad (27)$$

After some vector algebra this can also be written as

$$\begin{aligned} \frac{\partial}{\partial B_k^0} H^Z &= \frac{g_e}{2c} \left[\frac{1}{2} \sigma_k + \frac{K}{4} L_k + L_k \frac{K}{4} + \nabla \cdot \left(\frac{K-1}{4} \mathbf{r} \right) \sigma_k \right. \\ &\quad \left. - \nabla_k \left(\frac{K-1}{4} \boldsymbol{\sigma} \cdot \mathbf{r} \right) \right]. \end{aligned} \quad (28)$$

For the calculation of matrix elements for the last three operators one conveniently can use the turn-over rule, which will avoid the calculation of the gradient of the potential, which appears in K .

We end this section by a short remark on gauge invariance. In calculations we often have to approximate the wave function. As a result the calculated *g*-tensor will depend on the origin we have chosen for the magnetic vector field. But if the calculated Kramers pair Φ_1 and Φ_2 are exact eigenfunctions of the Hamiltonian H_0 , without magnetic field [see Eq. (21)], then the calculated *g*-values will be gauge invariant. We will show this gauge invariance for a particular gauge transformation, but similar arguments can be used for general gauge transformations. The discussion here is based on the treatment of Griffith (Ref. 23, Appendix 5). We will rederive it for the ZORA case. Suppose the vector field \mathbf{A}^0 has a different gauge origin compared to the one we used before, we have

$$\mathbf{A}^0 = \frac{1}{2} [\mathbf{B}^0 \times (\mathbf{r} - \mathbf{C})], \quad (29)$$

with \mathbf{C} some arbitrary constant vector, the new gauge origin. The derivative of the total Zeeman-Hamiltonian with respect to B_k^0 , Eq. (28), will have these extra terms

$$\begin{aligned} & - \frac{g_e}{2c} \left[\frac{K}{4} (\mathbf{C} \times \mathbf{p})_k + (\mathbf{C} \times \mathbf{p})_k \frac{K}{4} + \nabla \cdot \left(\frac{K-1}{4} \mathbf{C} \right) \sigma_k \right. \\ & \quad \left. - \nabla_k \left(\frac{K-1}{4} \boldsymbol{\sigma} \cdot \mathbf{C} \right) \right]. \end{aligned} \quad (30)$$

The matrix elements relevant for the calculation of the *g* tensor will be zero if we have exact eigenfunctions, since for $i, j = 1$ or 2 , the labels of the degenerate Kramers pair, with eigenvalue E_0

$$\begin{aligned}
0 &= i \frac{g_e}{4c} E_0 \langle \Phi_i | [\mathbf{C} \times \mathbf{r}]_k - [\mathbf{C} \times \mathbf{r}]_k | \Phi_j \rangle \\
&= i \frac{g_e}{4c} \langle \Phi_i | H_0 [\mathbf{C} \times \mathbf{r}]_k - [\mathbf{C} \times \mathbf{r}]_k H_0 | \Phi_j \rangle \\
&= i \frac{g_e}{4c} \langle \Phi_i | \boldsymbol{\sigma} \cdot \mathbf{p} \frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{p} [\mathbf{C} \times \mathbf{r}]_k \\
&\quad - [\mathbf{C} \times \mathbf{r}]_k \boldsymbol{\sigma} \cdot \mathbf{p} \frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{p} | \Phi_j \rangle \\
&= \frac{g_e}{4c} \langle \Phi_i | \boldsymbol{\sigma} \cdot \mathbf{p} \frac{K}{2} [\mathbf{C} \times \boldsymbol{\sigma}]_k + [\mathbf{C} \times \boldsymbol{\sigma}]_k \frac{K}{2} \boldsymbol{\sigma} \cdot \mathbf{p} | \Phi_j \rangle \\
&= -\frac{g_e}{2c} \langle \Phi_i | \frac{K}{4} (\mathbf{C} \times \mathbf{p})_k + (\mathbf{C} \times \mathbf{p})_k \frac{K}{4} \\
&\quad + \nabla \cdot \left(\frac{K-1}{4} \mathbf{C} \right) \sigma_k - \nabla_k \left(\frac{K-1}{4} \boldsymbol{\sigma} \cdot \mathbf{C} \right) | \Phi_j \rangle. \quad (31)
\end{aligned}$$

Thus we find that the matrix element of the extra terms found in Eq. (30) are zero, which proves the gauge invariance.

B. GIAO formalism

In the last section we saw that the results for the calculation of the g -tensor are gauge dependent, if one uses a finite basis set. A standard solution to this problem is the use of gauge including atomic orbitals (GIAO's),^{17,18} which is the subject of this section. We will consider the two spinors Φ_1 and Φ_2 of the last section, which are eigenfunctions of the Hamiltonian H_0 , without magnetic field [see Eq. (21)], with eigenvalue E_0 . The problem of gauge dependence has its origin in the fact that the two spinors Φ_1 and Φ_2 are not exact eigenfunctions of H_0 , they are only exact eigenfunctions of the matrix representation of H_0 in the basis used.

We assume that we have solved the spatial parts of these two spinors in a basis set consisting of atomic basis functions. Each atomic basis function is centered around one particular nucleus. $\Phi_{i\nu}$ is the contribution to the spinor i ($i = 1$ or 2) of basis functions that are centered around nucleus ν , thus

$$\Phi_i = \sum_{\nu} \Phi_{i\nu}. \quad (32)$$

We define field-dependent operators X_{ν} ,

$$X_{\nu}(\mathbf{B}^0) = \frac{i}{2c} (\mathbf{B}^0 \times \mathbf{R}_{\nu}) \cdot \mathbf{r} = \frac{i}{2c} \mathbf{B}^0 \cdot (\mathbf{R}_{\nu} \times \mathbf{r}). \quad (33)$$

Using these operators X_{ν} we make field-dependent Ψ_i 's, or GIAO's, Löwdin orthonormalized up to first order in the field \mathbf{B}^0 ,

$$\begin{aligned}
\Psi_i(\mathbf{B}^0) &= \Phi_i - \sum_{\nu} X_{\nu}(\mathbf{B}^0) \Phi_{i\nu} - \frac{1}{2} S_{1i}^1(\mathbf{B}^0) \Phi_1 \\
&\quad - \frac{1}{2} S_{2i}^1(\mathbf{B}^0) \Phi_2, \quad (34)
\end{aligned}$$

with S_{ij}^1 the part of the overlap matrix (before the Löwdin orthonormalization), which is first order in \mathbf{B}^0 ,

$$S_{ij}^1(\mathbf{B}^0) = \sum_{\mu\nu} \langle \Phi_{i\mu} | X_{\mu}(\mathbf{B}^0) - X_{\nu}(\mathbf{B}^0) | \Phi_{j\nu} \rangle. \quad (35)$$

$\Psi_{i\nu}$ is the contribution to the field-dependent spinor i ($i = 1$ or 2) of basis functions that are centered around nucleus ν ,

$$\Psi_{1\nu}(\mathbf{B}^0) = [1 - X_{\nu}(\mathbf{B}^0) - \frac{1}{2} S_{11}^1(\mathbf{B}^0)] \Phi_{1\nu} - \frac{1}{2} S_{21}^1(\mathbf{B}^0) \Phi_{2\nu}, \quad (36)$$

$$\begin{aligned}
\Psi_{2\nu}(\mathbf{B}^0) &= -\frac{1}{2} S_{12}^1(\mathbf{B}^0) \Phi_{1\nu} + [1 - X_{\nu}(\mathbf{B}^0) \\
&\quad - \frac{1}{2} S_{22}^1(\mathbf{B}^0)] \Phi_{2\nu}. \quad (37)
\end{aligned}$$

For the g -tensor we need to calculate

$$\begin{aligned}
g_{kx} &= 4c \operatorname{Re} \frac{\partial}{\partial B_k^0} \langle \Psi_1 | H_0 + H^Z | \Psi_2 \rangle |_{B^0=0} \\
&= 4c \operatorname{Re} \frac{\partial}{\partial B_k^0} \langle \Psi_2 | H_0 + H^Z | \Psi_1 \rangle |_{B^0=0}, \quad (38a)
\end{aligned}$$

$$\begin{aligned}
g_{ky} &= 4c \operatorname{Im} \frac{\partial}{\partial B_k^0} \langle \Psi_1 | H_0 + H^Z | \Psi_2 \rangle |_{B^0=0} \\
&= 4c \operatorname{Im} \frac{\partial}{\partial B_k^0} \langle \Psi_2 | H_0 + H^Z | \Psi_1 \rangle |_{B^0=0}, \quad (38b)
\end{aligned}$$

$$\begin{aligned}
g_{kz} &= 4c \operatorname{Re} \frac{\partial}{\partial B_k^0} \langle \Psi_1 | H_0 + H^Z | \Psi_1 \rangle |_{B^0=0} \\
&= -4c \operatorname{Re} \frac{\partial}{\partial B_k^0} \langle \Psi_2 | H_0 + H^Z | \Psi_2 \rangle |_{B^0=0}, \quad (38c)
\end{aligned}$$

Since now the Ψ_i 's also depend on the magnetic field the derivative becomes

$$\begin{aligned}
&\frac{\partial}{\partial B_k^0} \langle \Psi_i(\mathbf{B}^0) | H_0 + H^Z | \Psi_j(\mathbf{B}^0) \rangle |_{B^0=0} \\
&= \left\langle \Phi_i \left| H_0 \right| \frac{\partial \Psi_j(\mathbf{B}^0)}{\partial B_k^0} \right\rangle_{B^0=0} \\
&\quad + \left\langle \frac{\partial \Psi_i(\mathbf{B}^0)}{\partial B_k^0} \left| H_0 \right| \Phi_j \right\rangle_{B^0=0} \\
&\quad + \left\langle \Phi_i \left| \frac{\partial H^Z}{\partial B_k^0} \right| \Phi_j \right\rangle_{B^0=0}. \quad (39)
\end{aligned}$$

A useful relation is

$$\boldsymbol{\sigma} \cdot \mathbf{p} X_{\nu}(\mathbf{B}^0) = X_{\nu}(\mathbf{B}^0) \boldsymbol{\sigma} \cdot \mathbf{p} + \frac{1}{2c} [\mathbf{B}^0 \cdot (\mathbf{R}_{\nu} \times \boldsymbol{\sigma})]. \quad (40)$$

Define the operators $Y_{\nu k}$ and numbers T_{ij}^{1k} :

$$Y_{\nu k} \equiv \frac{\partial X_{\nu}(\mathbf{B}^0)}{\partial B_k^0} \Big|_{B^0=0} = \frac{i}{2c} [\mathbf{R}_{\nu} \times \mathbf{r}]_k, \quad (41)$$

$$T_{ij}^{1k} \equiv \left. \frac{\partial S_{ij}^1(\mathbf{B}^0)}{\partial B_k^0} \right|_{B^0=0} = \sum_{\mu\nu} \langle \Phi_{i\mu} | (Y_{\mu k} - Y_{\nu k}) | \Phi_{j\nu} \rangle - \frac{1}{2} T_{i1}^{1k} \langle \Phi_1 | H_0 | \Phi_j \rangle - \frac{1}{2} T_{i2}^{1k} \langle \Phi_2 | H_0 | \Phi_j \rangle + \left\langle \Phi_i \left| \frac{\partial H^Z}{\partial B_k^0} \right|_{B^0=0} \Phi_j \right\rangle. \quad (42)$$

Note that $T_{ij}^{1k} = (T_{ji}^{1k})^*$. Now we have

$$\left. \frac{\partial \Psi_{j\nu}(\mathbf{B}^0)}{\partial B_k^0} \right|_{B^0=0} = -Y_{\nu k} \Phi_{j\nu} - \frac{1}{2} T_{1j}^{1k} \Phi_{1\nu} - \frac{1}{2} T_{2j}^{1k} \Phi_{2\nu}. \quad (43)$$

Equation (39) becomes

$$\begin{aligned} \frac{\partial}{\partial B_k^0} \langle \Psi_i(\mathbf{B}^0) | H_0 + H^Z | \Psi_j(\mathbf{B}^0) \rangle \Big|_{B^0=0} \\ = - \sum_{\nu} \langle \Phi_i | H_0 Y_{\nu k} | \Phi_{j\nu} \rangle + \sum_{\mu} \langle \Phi_{i\mu} | Y_{\mu k} H_0 | \Phi_j \rangle \\ - \frac{1}{2} T_{1j}^{1k} \langle \Phi_i | H_0 | \Phi_1 \rangle - \frac{1}{2} T_{2j}^{1k} \langle \Phi_i | H_0 | \Phi_2 \rangle \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial B_k^0} \langle \Psi_i(\mathbf{B}^0) | H_0 + H^Z | \Psi_j(\mathbf{B}^0) \rangle \Big|_{B^0=0} \\ = \langle \Phi_i | \frac{\partial H^Z}{\partial B_k^0} | \Phi_j \rangle + \frac{1}{4c} \sum_{\lambda} \langle \Phi_{i\lambda} | -K[\mathbf{R}_{\lambda} \times \mathbf{p}]_k - i(K-1)(\boldsymbol{\sigma} \cdot \mathbf{R}_{\lambda}) \mathbf{p}_k + i(K-1) \sigma_k (\mathbf{R}_{\lambda} \cdot \mathbf{p}) | \Phi_j \rangle \\ + \frac{1}{4c} \sum_{\lambda} \langle \Phi_i | -[\mathbf{R}_{\lambda} \times \mathbf{p}]_k K + \mathbf{p}_k (\boldsymbol{\sigma} \cdot \mathbf{R}_{\lambda}) i(K-1) - (\mathbf{p} \cdot \mathbf{R}_{\lambda}) \sigma_k i(K-1) | \Phi_{j\lambda} \rangle \\ + \frac{i}{2c} \sum_{\lambda} \langle \Phi_{i\lambda} | [\mathbf{R}_{\lambda} \times \mathbf{r}]_k V + \mathbf{p} \cdot [\mathbf{R}_{\lambda} \times \mathbf{r}]_k \frac{K}{2} \mathbf{p} + \boldsymbol{\sigma} \cdot \left(\nabla \left([\mathbf{R}_{\lambda} \times \mathbf{r}]_k \frac{K-1}{2} \right) \times \mathbf{p} \right) | \Phi_j \rangle \\ - \frac{i}{2c} \sum_{\lambda} \langle \Phi_i | [\mathbf{R}_{\lambda} \times \mathbf{r}]_k V + \mathbf{p} \cdot [\mathbf{R}_{\lambda} \times \mathbf{r}]_k \frac{K}{2} \mathbf{p} + \boldsymbol{\sigma} \cdot \left(\nabla \left([\mathbf{R}_{\lambda} \times \mathbf{r}]_k \frac{K-1}{2} \right) \times \mathbf{p} \right) | \Phi_{j\lambda} \rangle \\ - \frac{iE_0}{2c} \sum_{\lambda} \langle \Phi_{i\lambda} | [\mathbf{R}_{\lambda} \times \mathbf{r}]_k | \Phi_j \rangle + \frac{iE_0}{2c} \sum_{\lambda} \langle \Phi_i | [\mathbf{R}_{\lambda} \times \mathbf{r}]_k | \Phi_{j\lambda} \rangle. \quad (46) \end{aligned}$$

This is in the form in which it is implemented. This equation can also be written in a form which shows explicitly its gauge invariance, since this expression only depends on differences of position vectors ($\mathbf{r}_{\nu} = \mathbf{r} - \mathbf{R}_{\nu}$)

$$\begin{aligned} \frac{\partial}{\partial B_k^0} \langle \Psi_i(\mathbf{B}^0) | H_0 + H^Z | \Psi_j(\mathbf{B}^0) \rangle \Big|_{B^0=0} \\ = \sum_{\lambda\nu} \langle \Phi_{i\lambda} | \frac{1}{2c} \sigma_k + \frac{K}{4c} [\mathbf{r}_{\lambda} \times \mathbf{p}]_k + [\mathbf{r}_{\nu} \times \mathbf{p}]_k \frac{K}{4c} | \Phi_{j\nu} \rangle + \sum_{\lambda\nu} \langle \Phi_{i\lambda} | i \frac{K-1}{4c} (\boldsymbol{\sigma} \cdot \mathbf{r}_{\lambda}) \mathbf{p}_k - i \frac{K-1}{4c} \sigma_k (\mathbf{r}_{\lambda} \cdot \mathbf{p}) | \Phi_{j\nu} \rangle \\ + \sum_{\lambda\nu} \langle \Phi_{i\lambda} | -\mathbf{p}_k (\boldsymbol{\sigma} \cdot \mathbf{r}_{\nu}) i \frac{K-1}{4c} + (\mathbf{p} \cdot \mathbf{r}_{\nu}) \sigma_k i \frac{K-1}{4c} | \Phi_{j\nu} \rangle + \sum_{\lambda\nu} \langle \Phi_{i\lambda} | -\frac{i}{4c} [\boldsymbol{\sigma} \cdot (\mathbf{R}_{\lambda} - \mathbf{R}_{\nu})] \mathbf{p}_k \\ + \frac{i}{4c} [\mathbf{p} \cdot (\mathbf{R}_{\lambda} - \mathbf{R}_{\nu})] \sigma_k | \Phi_{j\nu} \rangle + \frac{i}{2c} \sum_{\lambda\nu} \langle \Phi_{i\lambda} | [(\mathbf{R}_{\lambda} - \mathbf{R}_{\nu}) \times \mathbf{r}_{\lambda}]_k (V - E_0) + \boldsymbol{\sigma} \cdot \mathbf{p} [(\mathbf{R}_{\lambda} - \mathbf{R}_{\nu}) \times \mathbf{r}_{\lambda}]_k \frac{K}{2} \sigma \cdot \mathbf{p} | \Phi_{j\nu} \rangle \\ + \frac{i}{2c} \sum_{\lambda\nu} (\mathbf{R}_{\nu} \times \mathbf{R}_{\lambda}) \langle \Phi_{i\lambda} | V + \boldsymbol{\sigma} \cdot \mathbf{p} \frac{K}{2} \sigma \cdot \mathbf{p} - E_0 | \Phi_{j\nu} \rangle. \quad (47) \end{aligned}$$

Suppose Φ_i is the exact eigenfunction of the Hamiltonian H_0 , when the magnetic field is zero, then we are only left with the last term in this equation, since

$$\begin{aligned} E_0 \sum_{\mu\nu} \langle \Phi_{i\mu} | Y_{\mu k} - Y_{\nu k} | \Phi_{j\nu} \rangle - E_0 (\frac{1}{2} T_{1j}^{1k} \delta_{i1} + \frac{1}{2} T_{2j}^{1k} \delta_{i2} \\ + \frac{1}{2} T_{i1}^{1k} \delta_{j1} + \frac{1}{2} T_{i2}^{1k} \delta_{j2}) \\ = E_0 T_{ij}^{1k} - E_0 (\frac{1}{2} T_{ij}^{1k} + \frac{1}{2} T_{ij}^{1k}) = 0. \quad (45) \end{aligned}$$

In this case the result is exactly the same as when we would not use GIAO's. However, in general Φ_i will not be an exact eigenfunction, due to incompleteness of the basis set. Equation (44) can be rewritten as

TABLE I. Optimized Slater exponents for all electron calculations.

H		C		N	O	F	Ti			
1s	3.30	1s	12.00	12.85	13.25	15.00	1s	99.00	2p	16.90
1s	2.00	1s	6.85	7.65	8.30	9.40	1s	27.60	2p	9.75
1s	1.00	1s	4.90	5.75	6.55	7.45	1s	20.35	2p	6.85
1s	0.71	2s	5.95	6.85	7.05	3.60	2s	18.05	3p	4.95
2p	1.00	2s	2.70	3.20	3.20	2.33	2s	9.35	3p	3.35
2p	2.00	2s	1.75	2.05	2.05	1.70	2s	7.20	3p	2.25
3d	1.50	2s	1.25	1.40	1.50	1.00	3s	5.05	4p	2.00
3d	2.50	2p	5.15	6.10	5.70	6.78	3s	3.55	4p	1.00
		2p	2.40	2.95	3.05	3.66	3s	2.60	3d	6.45
		2p	1.30	1.60	1.65	1.94	4s	2.95	3d	3.35
		2p	0.78	0.94	1.00	1.15	4s	1.70	3d	1.70
		3d	1.50	1.50	1.50	1.50	4s	1.10	3d	0.90
		3d	2.50	2.50	2.50	2.50	4s	0.75	4f	2.00
		4f	2.00	2.00	2.00	2.00			4f	1.00
		4f	4.00	4.00	4.00	4.00				

To show that the last line in this equation is gauge invariant one has to use that the two spinors Φ_1 and Φ_2 are exact eigenfunctions of the matrix representation of the Hamiltonian H_0 [see Eq. (21)] in the used basis.

V. IMPLEMENTATION

The ADF (Amsterdam density functional) program²⁴ can perform electronic structure calculations on molecular systems. It performs self-consistent field calculations using density functional theory (DFT), solving the one-electron Kohn–Sham equations.

Results will be given using the local density approximation (LDA), with the parametrization of Vosko, Wilk, and Nusair²⁵ and gradient correction (GGC) terms added, Becke correction for exchange⁷ and the Perdew correction for correlation.⁸

The ADF program uses a Slater type orbital (STO) basis set and matrix elements are calculated by numerical integration. Use is made of the point group symmetry of the molecule. In the ZORA case, including spin–orbit coupling, double group symmetry adapted functions are used. See for more details concerning the implementation of ZORA in ADF Ref. 9 and references there in.

In ADF usually the frozen core approximation is used. If one wants to use this approximation in the ZORA case (including spin–orbit coupling) one should orthogonalize the basis functions on ZORA core orbitals. In the present implementation the basis functions are orthogonalized on scalar relativistic (SR) ZORA, i.e., ZORA without spin–orbit coupling, core orbitals. In the spherical case for light atoms, the spin–orbit split (ZORA) eigenfunctions have almost the same radial behavior as the SR ZORA orbitals, the difference is then only in the spin and angular part. If this is the case, then for closed shell cores there is no difference whether one uses SR ZORA or ZORA orbitals, because they span the same space.

In the present implementation in ADF it is assumed that the Kramers doublet will completely determine the

g -tensor. No spin-polarization effects are included.

For the formulation using a single gauge origin, ADF is extended so that it can calculate the real numbers g_{ij} in Eq. (26), using the operator in Eq. (28). For the GIAO method Eqs. (38) and (46) are used. In both formulations from the real numbers g_{ij} a true tensor is made according to Eq. (24). The eigenvectors of this tensor, which are the principal axes of the g tensor, and the eigenvalues, which are the squares of the g values, are calculated. For the calculation of matrix elements sometimes the turn-over rule is used, if it avoids the calculation of the gradient of the potential. The new part of the code is parallelized along the lines of the existing parallelization in the ADF program.

VI. RESULTS

The g -values of some small molecules are calculated, to test the method developed in this article, using the zero order regular approximation (ZORA). We have chosen for NO₂, HCO, and TiF₃ since the g -values of these molecules were calculated recently with other methods,^{5,26–28} which all use the Pauli approximation for the relevant terms.

For NO₂ and HCO, the experimental geometry²⁹ was used in the calculations. For TiF₃ a ZORA optimized structure was taken, with D_{3h} symmetry, which gave for LDA a Ti–F distance of 1.751 Å, and for GGC a Ti–F distance of 1.780 Å. The z axis was chosen to be axis of highest symmetry. The planar molecules NO₂ and HCO are placed in the yz plane. The standard basis sets II and V of the ADF program have a 1s frozen core for C, N, O, and F and 1s, 2s, 2p frozen core for Ti.

Basis set II is a double- ζ STO basis set, and basis set V is triple- ζ for the valence orbitals plus two polarization functions. Basis set IV for Ti is double- ζ for 3s and 3p, triple- ζ for 4s and 3d and has one 4p polarization function. The all-electron basis sets are given in Table I, which are quadruple- ζ for the valence orbitals and have four polarization functions.

TABLE II. g -values from ZORA-GGC spin-restricted calculations.

	g_{xx}	g_{yy}	g_{zz}
NO₂			
Basis set II			
GIAO	2.007 2	1.985 5	2.001 6
single gauge origin	2.008 8	1.985 5	2.001 8
Δg origin (1,1,1)	0.000 06	0.000 04	0.000 03
Δg origin (10,10,10)	0.000 63	0.000 36	0.000 29
basis set V			
GIAO	2.007 2	1.985 9	2.001 6
single gauge origin	2.007 4	1.985 8	2.001 7
Δg origin (1,1,1)	0.000 10	0.000 02	0.000 00
Δg origin (10,10,10)	0.001 05	0.000 24	0.000 04
all electron basis set			
GIAO	2.007 3	1.986 3	2.001 6
single gauge origin	2.007 3	1.986 3	2.001 6
Δg origin (1,1,1)	0.000 02	0.000 00	0.000 00
Δg origin (10,10,10)	0.000 21	0.000 03	0.000 00
HCO			
basis set II			
GIAO	2.005 2	2.002 1	1.990 1
single gauge origin	2.005 5	2.002 1	1.990 3
basis set V			
GIAO	2.005 5	2.002 1	1.989 9
single gauge origin	2.005 5	2.002 1	1.989 9
all electron basis set			
GIAO	2.005 6	2.002 1	1.990 0
single gauge origin	2.005 6	2.002 1	1.990 0
TiF₃			
basis set II			
GIAO	1.921 4	1.921 4	2.001 1
single gauge origin	1.920 4	1.920 4	2.001 2
F basis set V, Ti basis set IV			
GIAO	1.927 2	1.927 2	2.001 3
single gauge origin	1.927 2	1.927 2	2.001 3
all electron basis set			
GIAO	1.922 5	1.922 5	2.001 2
single gauge origin	1.922 5	1.922 5	2.001 2

In Table II results are given for the g -values of these molecules comparing the different basis sets and comparing the GIAO method with the single gauge origin formulation. Already the smallest frozen core basis set used, gives reasonable results compared to the large all electron basis set. Thus the frozen core approximation is not a severe approximation for the calculation of the g values. The largest effect of the basis set is for TiF_3 , but there the deviation of the g -values with respect to the free electron value is also largest.

Since we only have a finite basis set, we only have approximate eigenfunctions, and the calculated g -values will be gauge dependent in the single gauge origin formulation. As in Refs. 26 and 30 the gauge dependence was tested by shifting the gauge origin. Here we can also test it by comparison with the gauge-independent GIAO values.

For NO_2 the gauge origin was chosen to be at the position of the N nucleus, for HCO at the position of the C nucleus and for TiF_3 it was at the position of the Ti nucleus. We shift this gauge origin to the (1,1,1) and the (10,10,10) position in a.u., compared to the original position. The effect of these two shifts on the g -values of NO_2 can be found in Table II for the different basis sets used. As can be expected

the gauge dependence of the results is smallest for the largest basis set. Compared to the results of Lushington *et al.*^{26,30} for the NO_2 molecule, our calculated gauge dependence is smaller, perhaps due to the fact that we use Slater type orbitals, instead of Gaussian type orbitals. The shift of (1,1,1) bohr, which is of the order of the size of the NO_2 molecule gives some hint for the gauge dependence of our results, and a shift of the origin with (10,10,10) bohr may give some idea how large it can be in larger molecules. A better test of the gauge dependence is to compare the results with those of the GIAO method. Except for the results for NO_2 using basis set II, the gauge dependence of the g -values for the three test molecules using basis set II and V is smaller than the remaining basis set effect. The relatively large effect for NO_2 is probably related to the fact that the density of the unpaired electron is more spread over the whole molecule than it is for the other two test molecules. Although one needs to calculate many more matrix elements for the GIAO method than for the single gauge origin formulation, once implemented, it is more satisfactory to use the GIAO method, since it is gauge invariant from the start.

In Table III our best LDA and GGC results are shown,

TABLE III. Calculated Δg -values ($\Delta g = g - g_e$) from all electron spin-restricted ZORA calculations in comparison with experiment and some recent calculations.

	$\Delta g_{xx} \times 10^4$	$\Delta g_{yy} \times 10^4$	$\Delta g_{zz} \times 10^4$	
NO₂				
Experiment (Ref. 33)	39	-113	-3	
Restricted LDA	49	-167	-6	
Restricted GGC	50	-160	-6	
Restricted GGC ^a	50	-164	-6	
Spin-unrestricted GGC ^a	42	-138	-8	
ROHF (Ref. 5)	47	-119	4	
ROHF (Ref. 30)	23	-66	-5	
CI (Ref. 27)	36	-103	-5	
HCO				
Experiment (Ref. 34)	14	0	-75	
Restricted LDA	33	-2	-142	
Restricted GGC	33	-2	-123	
Restricted GGC ^a	32	-1	-124	
Spin-unrestricted GGC ^a	27	-3	-97	
ROHF (Ref. 5)	18	1	-55	
TiF₃				
Experiment (Ref. 31)	-1113	-1113	-111	neon (site a)
	-1215	-1215	-111	neon (site b)
	-1237	-1237	-37	argon
Restricted LDA	-848	-848	-14	
Restricted GGC	-797	-797	-10	
Restricted GGC ^a	-733	-733	1	
Spin-unrestricted GGC ^a	-428	-428	-17	
Restricted LDA (Ref. 28)	-956	-956	-3	
Restricted GGC (Ref. 28)	-778	-778	3	
Spin-unrestricted GGC (Ref. 28)	-975	-975	5	

^aCalculations were done using the program of Ref. 4 (see the text).

using the large all-electron basis set. To the accuracy shown the GIAO method and the single gauge origin formulation give the same results. The LDA and GGC results are close and show fair agreement with experimental data. In Ref. 31 results are shown of experiments, where TiF₃ was trapped in neon and argon matrices.

The scaled ZORA energy expression, using the approximation of Eq. (25), gave an isotropic decrease of the g values compared to the ZORA value of approximately 0.0001 for all the calculated g -values of the three test molecules. Since this is such a small difference we only show the scaled ZORA g -values in the tables.

Very recently⁴ a program was developed by Schreckenbach and Ziegler for the calculation of the g -tensor, using second order perturbation theory, DFT and the GIAO method. In this program, which is also an extension of the ADF program (as is our implementation), relativity can be taken into account using the Pauli-Hamiltonian. Calculations were reported for some small radicals, including NO₂ and HCO, and some other compounds. Schreckenbach and Ziegler generously made this program available to us, so that now we can compare it with our method. We used this program to calculate the g -tensors for the same test molecules using the standard ADF basis set IV for Ti, and basis sets V for H, C, N, and O, and the same geometries. Results of these calculations using the Pauli-Hamiltonian are shown in Table III. The spin-restricted results are in close agreement with our results. For NO₂ and HCO the spin-unrestricted

results are in better agreement with experiment, but for TiF₃ the spin-restricted are better.

The close agreement for the spin-restricted results between the different methods could be expected, since for these light elements relativity does not play a very important role and the two approximate relativistic Hamiltonians, the Pauli and ZORA Hamiltonian, will not give very different results. Moreover, for these molecules there is a small effect of spin-orbit coupling and this effect can be taken into account in first order without much loss of accuracy compared to taken it into account to all orders. For the Pauli-Hamiltonian problems may arise if one wants to take spin-orbit coupling variationally into account, since the spin-orbit operator in the Pauli approximation behaves as an attractive $-r^{-3}$ potential close to the nucleus, which can lead to arbitrarily large negative energies in a self-consistent equation. In Ref. 28 Belanzoni *et al.* reported density functional calculations for the g -tensors (and A-tensors) of TiF₃, using second order perturbation theory. Their results for the spin-restricted LDA and GGC calculations are in close agreement with our results, although they used a model with spin-orbit coupling parameters derived from atomic calculations, and start with a nonrelativistic equation. In their method they had to choose the atomic configuration from which to determine the spin-orbit parameters. In our method the spin-orbit coupling is automatically taken into account, without any arbitrariness. Moreover our method may be used for heavier systems, where relativistic effects are of importance.

Note that the effects of spin-polarization for TiF_3 if we compare the results of Ref. 28 with the results using the program of Ref. 4 are of opposite sign. This difference has its origin in the way the orbital energy differences are calculated in the sum-over-states expression. In Ref. 4 they are calculated using the orbital energies of electrons with the same spin, whereas in Ref. 28 some effect of the orbital energy of the other spin is included.

In our calculations we did not take spin-polarization effects into account. These effects are interesting, since as we saw they may improve the results. A possible way^{10,11} to include spin-polarization effects in spin-orbit coupled equations will lead to off-diagonal elements in the exchange-correlation potential, leading to more complicated equations than solved in this paper.

Next we compare our results with recent *ab initio* results from the literature in Table III. In Ref. 5 Ishii *et al.* performed *ab initio* calculations, where finite perturbation theory was compared with second order perturbation theory. In these standard approaches the effect of spin-orbit coupling was only taken into account in first order. For NO_2 and HCO they obtained results of similar accuracy compared to experiment as our results, although their results depended somewhat on the method used. In Table III we show their results using finite perturbation theory at the restricted open shell Hartree-Fock (ROHF) level. They also calculated separately the contribution of the one- and two-electron spin-orbit coupling terms. The one-electron term is the spin-orbit interaction due to the Coulomb field of the nucleus. The first part of the two-electron terms is the spin-orbit interaction due to the Coulomb field of the electrons, a term analogous to the one-electron term, called electron-electron spin-orbit interaction in Ref. 2. The other part of the two-electron terms is the spin-other orbit interaction. In our calculations the electron-electron spin-orbit interaction is explicitly taken into account. In DFT the spin-other orbit interaction should be included in the exchange-correlation potential, but since we are using nonrelativistic approximations for this potential, we may not expect that this term is already included. Unfortunately in Ref. 5 both two-electron terms are called spin-other orbit coupling terms. In Ref. 30 *ab initio* calculations were performed, where besides these spin-orbit coupling terms, also the spin Zeeman kinetic-energy correction and the one- and two-electron spin-orbit Zeeman gauge corrections were taken into account. In our calculations we use the regular approximation (ZORA) for these terms (see Sec. II).

In Ref. 27 *g*-tensor calculations were reported at the multireference CI level. The results for NO_2 showed a considerable improvement over the ROHF results, and can be considered as the best *ab initio* calculations so far. Our spin-restricted results for NO_2 are of comparable accuracy as the ROHF results, and there is thus still room for improvement. As was remarked before one would like to incorporate spin-polarization effects, since they may improve upon the results (see Table III). The exchange-correlation functionals used may also be not accurate enough. For example, the applied exchange-correlation potentials have the wrong asymptotic

behavior in the outer region of the molecule,³² which is important for the unpaired electron. This will have an effect on the importance of spin-orbit coupling for the unpaired electron and therefore on the calculated *g*-values.

VII. CONCLUSIONS

Relativistic regular approximated (ZORA) expressions for magnetic interactions were derived and applied to the calculation of the interaction of an external homogeneous magnetic field and a paramagnetic molecule, which has a Kramers doublet ground state. Spin-orbit coupling was taken into account variationally, since it can be relatively large for these open shell molecules. For example for transition metal complexes, for which we want to use this method, it can be as important as the ligand-field splittings. The typical Zeeman interactions are much smaller, and we only calculated their effect on the energy, using the two degenerate Kramers spin-orbitals. Since our method includes the spin-orbit coupling (and other relativistic effects) in the self-consistent field DFT calculation, and uses first order perturbation theory for the Zeeman terms in the Hamiltonian, it is not much more expensive than an ordinary DFT calculation on a molecule without external field, and can easily be used for larger molecules.

The gauge dependence of the results using the single gauge origin formulation was tested by comparing it with the GIAO method and for NO_2 also by shifting the gauge origin for the magnetic field. Although the gauge dependence was small, it is more satisfactory to use the GIAO method, since it is gauge invariant from the start.

The calculated *g*-values, using DFT, of the test molecules NO_2 , HCO , and TiF_3 showed reasonable agreement with experimental data. The GGC results, using the Becke correction for exchange⁷ and the Perdew correction for correlation,⁸ were close to the LDA results. In the future we also plan to investigate what the effects are of taking spin-polarization in spin-orbit coupled density functional calculations into account; these were not included in the present paper.

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